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MAGNETIC EXCITATIONS IN MIXED VALENT MATERIALS

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ABSTRACT

The spin dynamics of a number of mixed valent materials have now been extensively studied using varied experimental probes including EPR, Raman scattering, infrared spectroscopy and inelastic neutron scattering. In this paper we review briefly photon and neutron spectroscopic studies of the 7F_0 - 7F_1 magnetic excitation dynamics in semiconducting SmS, SmSe and SmTe. New results for the phonon dispersion relations in SmS are presented. We also discuss recent neutron scattering experiments by Axe, Lawrence, Parks and ourselves on the γ - α transition in Ce.₇₄Th.₂₆. It is found that the spin fluctuation energy evolves from ~20 to >70 meV in going from the γ to the α phase.

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I INTRODUCTION

In the past two years the magnetic excitations in mixed valent materials have been probed by a variety of experimental techniques. The most direct of these is inelastic magnetic neutron scattering¹ which in the most favorable situations allows a complete study of the generalized susceptibility $\text{Im}\chi(\vec{Q},\omega)$ for wave vectors throughout the Brillouin zone and for energies ranging typically from 0.1 to 100 meV. The generalized spin susceptibility, in turn provides important space and time dependent information about the microscopic electronic states of the system. In this paper we review recent neutron and optical studies of two model mixed-valent materials, SmS and $\text{Ce}_{1-x}\text{Th}_x$. Both of these have been extensively discussed in the literature and indeed, in the proceedings of this conference itself, so we shall not discuss the relevant background in any detail.

For our purposes it is sufficient to note that at room temperature SmS, which has the rock-salt structure, is a magnetic semiconductor in which the Sm^{2+} ion has a well defined $4f^6$ configuration. At ~6.5 kBar it undergoes a strongly first order isostructural phase transition to a mixed valent state.² $\text{Ce}_{1-x}\text{Th}_x$ for $x \approx 0.265$, on the other hand, has a second, or nearly second order, phase transition as a function of temperature from the fcc γ to the fcc α phase;³ here $T_c(0.265) \approx 148$ K. $\text{Ce}_{.74}\text{Th}_{.26}$ is a good metal in both phases; further, as we shall show, the Ce ion also seems to exhibit mixed-valent characteristics in both phases albeit with markedly different spin fluctuation energies. Thus although these two materials represent archetypes of mixed-valence phenomena, they are in fact quite different in their details and hence offer an interesting contrast. We begin with a discussion of the magnetic exciton dynamics in the semiconducting phase of SmS.

II SmS

We consider firstly the electronic energy levels and concomitant magnetic exciton dynamics in semiconducting SmS. For an assemblage of $\text{Sm}^{2+}(4f^6)^7F$ ions the Hamiltonian may be written

$$H = \Delta \sum_i \vec{L}_i \cdot \vec{S}_i + \sum_i H_{\text{CEF},i} - 2 \sum_{i>j} J_{ij} \vec{S}_i \cdot \vec{S}_j, \quad (1)$$

where Δ is the spin-orbit coupling constant, H_{CEF} is the SmS cubic-crystal-field Hamiltonian, and J_{ij} is the isotropic exchange coupling between the Sm^{2+} spins i and j . In this case, Eq. (1) is best treated by diagonalizing each term in succession. Diagonalization of the spin-orbit coupling term yields the 7F_0 atomic manifold lowest, 7F_1 at energy Δ , 7F_2 at energy 3Δ , etc. In the free ion⁸ $\Delta = 422^\circ\text{K}$ so that for measurements below room temperature one need only consider the 7F_0 and 7F_1 J-manifolds. In SmS, because of the

Oh symmetry, the crystal-field term H_{CEF} will couple the 7F_0 and 7F_1 manifolds to the higher J-multiplets but it will not lift the 7F_1 triple degeneracy. The change in $E({}^7F_1) - E({}^7F_0)$ due to H_{CEF} in SmS is almost certainly less than 10 K.

The exchange term $J_{ij} \vec{S}_i \cdot \vec{S}_j$ serves to couple the ${}^7F_0 \rightarrow {}^7F_1$ ionic excitations on sites i and j. Thus, the single-ion transition becomes a propagating excitation in the crystal. Indeed, it corresponds almost exactly to the idealized singlet-triplet model which has been discussed extensively in the literature.⁴ Using the value $\langle {}^7F_1 | S | {}^7F_0 \rangle = 2$, the ${}^7F_0 \rightarrow {}^7F_1$ singlet-triplet dispersion relation within the MF-RPA approximation is given by⁵

$$\hbar\omega(\vec{k}) = \Delta [1 - 16R(T)J(\vec{k})/\Delta]^{1/2}. \quad (2)$$

where

$$J(\vec{k}) = \sum_j J_{ij} \exp [i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)]$$

and

$$R(T) = \frac{1 - \exp(-\Delta/k_B T)}{1 + 3 \exp(-\Delta/k_B T)}$$

For a paramagnet this mode is triply degenerate. Since the 7F_0 state is coupled to 7F_1 by both L and S this mode is magnetic-dipole active. Indeed these excitations have now been studied by each of inelastic neutron scattering, Raman scattering and far-infrared absorption.⁶

We show in Fig. 1 the magnetic exciton dispersion relations as measured by Shapiro, Birgeneau and Bucher⁵ using inelastic magnetic neutron scattering. The solid line through the $T=77$ K data represents the results of a least-squares fit of Eq. (2) to the measured energies. The spin Hamiltonian parameters so obtained are $\Delta=36.2 \pm 0.2$ meV, $J_1=0.043 \pm 0.003$ meV, $J_2=-0.025 \pm 0.007$ meV and $J_3=-0.003 \pm 0.001$ meV. The dot and dot-dashed lines represent calculated dispersion relations at $T=197$ K and $T=273$ K respectively. The agreement is excellent, thus confirming that in this weak-exchange regime the RPA works very well. Measurements of the $k=0$ exciton energies as a function of temperature have been obtained by Nathan et al.⁶ in each of SmS, SmSe, and SmTe using optical techniques. Their results are shown in Fig. 2. The solid lines represent fits of Eq. (2) at $k=0$ assuming the validity of the RPA theory. Nathan et al. have fixed Δ at the free ion value of $293.5 \text{ cm}^{-1}=36.4$ meV and they note that good fits can be obtained for a range of Δ of ± 0.5 meV. The results for the exchange are given in Table I. The neutron and optical results are in quite good agreement for SmS. In all three materials the spin orbit coupling constant is identical to that of free ion Sm^{++} to within the errors. This might be considered somewhat surprising given the close proximity of the

Fig. 1 - Dispersion relations of the $\text{Sm}^{2+}(4f^6) {}^7F_0-{}^7F_1$ singlet-triplet excitons at 77, 197 and 273 K. The lines are theoretical curves as described in the text. Figure taken from Ref. 5.

Fig. 2 - Magnetic exciton energy at $k=0$ as a function of temperature in SmS, SmSe, and SmTe. The solid lines are fits to Eq. (2) with $\Delta=293.5 \text{ cm}^{-1}=36.4 \text{ meV}$. Figure taken from Ref. 6.

TABLE I

Exchange interactions, measured and calculated static Van Vleck susceptibilities in the Samarium Chalcogenides

Material	16 J(0) (meV)	χ calc (cm ³ /mole)	χ meas (cm ³ /mole)	Ratio
SmS	10.9(optical) 9.6 (neutron)	9.72	9.15	1.06
SmSe	5.7 (optical)	8.42	7.85	1.07
SmTe	2.0 (optical)	7.55	7.0	1.08

pressure-driven mixed valent phases.

From the same mean field theory one obtains for the static susceptibility at T=0

$$\chi = 8 N \mu_B^2 / (\Delta - 16 J(0)) \quad (3)$$

We compare in Table I the measured Van Vleck susceptibilities² with those calculated from Eq. (3) using Δ , J(0) deduced from the magnetic excitons. The calculated susceptibility in all cases is about 7% higher than the measured value. Since Eq. (3) is based on free ion wave functions this may simply imply that the matrix element $\langle 1|L + 2S|0 \rangle$ which equals 2 for the free ion is ~2.07 in these chalcogenides due to covalency effects.

As discussed by a number of authors the exchange interactions in these materials are quite similar to those in the europium chalcogenides⁵⁻⁷ and undoubtedly arise from the same microscopic origins. It is of interest to note that Birgeneau et al. and Mehran et al.⁷ have deduced the $\text{Eu}^{++}\text{-Sm}^{++}$ exchange from Eu^{++} impurity spin resonance. An examination of Table IV of Ref. 7 shows that the $\text{Sm}^{++}\text{-Eu}^{++}$ net exchange is ~70% of the $\text{Sm}^{++}\text{-Sm}^{++}$ exchange in each system.

In order to complete the empirical characterization of SmS we have also carried out some limited measurements of the phonon dispersion relations at room temperature. The results are shown in Fig. 3. Unfortunately because of the intensity limitations we were unable to measure the LO branch, which according to recent theory, may play an important role in the semiconductor-metal transition. We note that the $k=0$ transverse optic mode is at an energy identical to that in EuS. For EuS the LO mode is around 33.0 meV, very near to the ${}^7F_0\text{-}{}^7F_1$ magnetic excitons already measured. These

Fig. 3 - Phonon dispersion relations in SmS at atmospheric pressure at $T=300$ K. The ordinates are in fcc reciprocal lattice units ($2\pi/a$).

modes thence could exhibit interesting interaction effects. Unfortunately, we will have to await the availability of a rather large isotope-enriched single crystal before these measurements will be feasible.

In summary, the dynamics and general magnetic properties of semiconducting SmS, SmSe and SmTe are now quite well understood. The most remarkable result is that the behavior is quite simple; there are no obvious precursive effects of the incipient pressure-driven mixed valent transitions.

III $\text{Ce}_{1-x}\text{Th}_x$

The element cerium is perhaps the most thoroughly studied of the rare earth mixed valent systems. At room temperature as a function of pressure cerium exhibits a first order isostructural

phase transition from the fcc γ phase to the more compact fcc α phase.⁸ It has been assumed that in the γ phase Ce is essentially integral valent with configuration $4f^1$ and that the transition corresponds to a partial delocalization ($4f \rightarrow 5d$) of this single $4f$ electron. The first order transition line in cerium terminates at a critical point at $P \sim 18$ kBar, $T \sim 600$ K. Similar effects may be obtained by alloying cerium with the quadrivalent element thorium. As discussed most recently by Parks and Lawrence,³ in $Ce_{1-x}Th_x$ the first order phase line terminates at a critical point defined by $T = 148$ K, $x_0 = 0.265$. This alloy then is much easier to study experimentally since one avoids the simultaneous complications of high pressures and high temperatures. Recently, Axe, Parks, Lawrence and the authors⁹ have carried out an extensive neutron scattering investigation of $Ce_{.74}Th_{.26}$ and in this section we summarize some of their salient results. In a cubic paramagnet the magnetic neutron scattering cross section may be written

$$\frac{d^2\sigma}{d\Omega d\omega} = \left(\frac{ye^2}{m_e c^2} \frac{g}{2}\right)^2 \frac{k_f}{k_i} |f(\vec{Q})|^2 2S^{zz}(\vec{Q}, \omega)$$

where

$$\begin{aligned} S^{zz}(\vec{Q}, \omega) &= \frac{1}{2\pi} \int dt \sum_{\vec{r}} e^{i(\vec{Q} \cdot \vec{r} - \omega t)} \langle S_O^z(0) S_{\vec{r}}^z(t) \rangle \\ &= \frac{kT}{g^2 \mu_B^2} \chi^{zz}(\vec{Q}) \frac{\hbar\omega/k_B T}{(1 - e^{-\hbar\omega/k_B T})} F^{zz}(\vec{Q}, \omega) \\ &= \frac{\hbar}{\pi} \frac{1}{g^2 \mu_B^2} (n(\omega) + 1) \text{Im} \chi^{zz}(\vec{Q}, \omega) \end{aligned} \quad (4)$$

where the symbols have their usual meaning.¹ Note that by definition $S^{zz} = S^{xx} = S^{yy}$. In the above we have assumed that the spatial part of the wave function, given in Fourier transform by the form factor $f(\vec{Q})$, is factorizable from the spin density operator $\vec{S}_Q(0)$ (for a rare earth $\vec{S} \rightarrow \vec{J}$ the total angular momentum). We remind the reader in addition that if the spin dynamics are purely relaxational, $F(\vec{Q}, t) \sim e^{-\Gamma(\vec{Q})t}$, then

$$F(\vec{Q}, \omega) = \frac{1}{\pi} \frac{\Gamma(\vec{Q})}{(\omega^2 + \Gamma^2(\vec{Q}))} \quad (5)$$

In Fig. 4 we show the lattice constant vs. temperature behavior obtained by Shapiro et al.⁹ in their polycrystalline $Ce_{.74}Th_{.26}$ sample. There is a small first order jump at $T = 153.5$ K on heating and at $T = 148$ K on cooling but the transition is nearly continuous. A simple linear interpolation (Vegard's Law) implies that the $4f$ -occupancy changes from $4f^{.83}$ at 300 K to $4f^{.71}$ just above the transition to $4f^{.61}$ just below the transition to $4f^{.44}$ at 10 K. Here the largest uncertainty is in the absolute value of the valency; the relative values should be rather more accurate. The $4f$ -

Fig. 4 - Lattice parameter versus temperature in $\text{Ce}_{0.74}\text{Th}_{0.26}$. The inset shows the observed hysteresis in the transition region. Figure taken from Ref. 9

Fig. 5 - Temperature dependence of $\text{Im}\chi(\vec{Q},\omega)$ for $\text{Ce}_{0.74}\text{Th}_{0.26}$. The low energy $\hbar\omega < 30$ meV data were taken at $Q = 1.5 \text{ \AA}^{-1}$ while for $\hbar\omega > 25$ meV data were taken at $Q = 3.0 \text{ \AA}^{-1}$. The data were matched in the overlapping region with the scaling factor deduced from Fig. 6. This procedure is justified by the fact that the shape of $\text{Im}\chi$ is Q -independent in this Q -region. Figure taken from Ref. 9

occupancy thus seems to be non-integral valent at all temperatures. The inelastic measurements turn out to be rather complicated because of phonon effects and because of the polycrystalline nature of the sample. These complications are discussed in detail by Shapiro et al.⁹ and we limit ourselves here to a brief presentation of their final results. The reader is referred to their paper for the details, especially vis-a-vis possible caveats. Fig. 5 gives the resultant $\text{Im}\chi(\vec{Q},\omega)$ in $\text{Ce}_{0.74}\text{Th}_{0.26}$ at five temperatures from 100 K to 250 K obtained on heating. The associated form factor squared for $E=30$ meV is given in Fig. 6. The data in Fig. 5 correspond to an average over the Brillouin zone although, as discussed by Shapiro et al., $\text{Im}\chi$ is at best weakly Q -dependent.

It may be seen instantly that $\gamma\text{Ce}_{1-x}\text{Th}_x$ differs significantly from semiconducting SmS. In a cubic system the $4f^1 2F_{5/2}$ manifold splits into a Γ_7 doublet and a Γ_8 quartet.¹⁰ Point charge estimates indicate a possible splitting of 10 meV. Thus for a conventional integral valent Ce^{3+} system one would expect to see sharp Γ_7 - Γ_8 crystal field excitons in direct analogy to the $7F_0$ - $7F_1$ excitons in SmS. Instead, even far from the critical point, one observes a purely Lorentzian response, that is, $\text{Im}\chi(\vec{Q},\omega) \rightarrow \omega/(\omega^2 + \Gamma^2)$. The solid lines represent a fit to this functional form. From Fig. 5 it may be seen that $\hbar\Gamma$ increases gradually from ~18 meV to ~23 meV as one approaches the first order line at 153.5 K. There is then a precipitous increase in the spin fluctuation energy to ~70 meV in the α phase. The form factor measurements in Fig. 6 demonstrate that the spin fluctuations are dominated by the $4f^1$

Fig. 6 - Intensity at an energy transfer of 30 meV vs. Q . The solid line is the $4f^1$ form factor squared with an arbitrary scaling factor. Figure taken from Ref. 9.

part of the wave function.

As discussed by Shapiro et al.⁹ a more detailed examination of these results shows that $\text{Im}\chi(Q, \omega)$ is at best weakly Q -dependent and further that $\chi(Q)$ deduced from Fig. 5 is completely consistent with the static susceptibility measurements of Parks and Lawrence.³ Thus all of the available data on $\text{Ce}_{1-x}\text{Th}_x$ are internally consistent. They demonstrate then that: (a) this is a local transition; (b) $\text{Ce}_{1-x}\text{Th}_x$ is in some sense mixed-valent in both the γ and α phases; (c) the most dramatic difference between the γ and α phases is the spin fluctuation energy, ~ 20 meV in the former and > 70 meV in the latter. These results are also quite similar to those in pure cerium in the γ and α phases although these latter experiments are rather less complete.¹¹ There is, as yet, no adequate theory for the mixed valent state.¹² However these neutron scattering measurements now give an energy scale for the spin fluctuation energies which can be related to f -band-widths, etc. in any proper theory. We refer the reader to the paper by Shapiro et al.⁹ for some speculative ideas along these lines.

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